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Synthesis of Highly Stable 1,3-Diaryl-1*H*-1,2,3-triazol-5-ylidenes and their Applications in Ruthenium-Catalyzed Olefin Metathesis

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Abstract

The formal cycloaddition between 1,3-diaza-2-azoniaallene salts and alkynes or alkyne equivalents provides an efficient synthesis of 1,3-diaryl-1*H*-1,2,3-triazolium salts, the direct precursors of 1,2,3-triazol-5-ylidenes. These N,N-diarylated mesoionic carbenes (MICs) exhibit enhanced stability in comparison to their alkylated counterparts. Experimental and computational results confirm that these MICs act as strongly electron-donating ligands. Their increased stability allows for the preparation of ruthenium olefin metathesis catalysts that are efficient in both ring-opening and ring-closing reactions.

Keywords

Stable carbenes; ligands; mesoionic compounds; ruthenium; olefin metathesis; cycloaddition; 1,3-diaza-2-azoniaallene salts; ring-closing metathesis; ring-opening metathesis

Introduction

Since their isolation a little more than two decades ago,[1] cyclic diamino carbenes of type **A** (Scheme 1), also referred to as N-heterocyclic carbenes (NHCs), have gained a privileged status among ancillary ligands for transition metals.[2] Particularly successful catalysts, incorporating these ligands, have been developed for olefin metathesis (e.g. **E**), [3] cross-couplings, [4] conjugate additions, [5] telomerization reactions,[6] and more recently for the gold-mediated electrophilic activation of alkenes, allenes and alkynes.[7] Integral to the success of these catalysts are the strong donating properties of carbenes, the strength of the resulting carbon-metal bonds, and their particular steric properties.[8] Besides the given properties of any ligand, an implied prerequisite is that the desired catalytically active complexes are synthetically accessible, and thus available in useful quantities for the necessary screening and optimization of the investigated methodologies. Therein lies a pivotal element to the

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Supporting Information **Available:** Full experimental details including synthesis, characterization and X-ray data. This material is available free of charge via the Internat at http://pubs.acs.org.

success of NHC-based catalysts: NHC complexes are simply and easily prepared by ligand substitution of a suitable transition-metal precursor with the stable free NHCs. Other synthetic avenues are available when direct ligand substitution fails, including C–X or C–H insertions,[9] and the use of carbene transfer reagents (e.g. CO_2 or Ag(I) adducts). [8c,10] However, the former route remains the most versatile and broadly applicable method to access the target metal carbene complexes. This readily explains the slower progress in the development of catalysts based on abnormal NHCs **B** (*a*NHCs), remote NHCs (*r*NHCs),[8c,11] or other non-traditional carbenes,[12] which only recently have become available as stable metal-free species. Evidently, the stability of the free carbenes is also of the utmost importance for applications in organocatalysis.[13]

In 2010, we reported the preparation of stable free mesoionic carbenes (MICs), 1*H*-1,2,3-triazol-5-ylidenes **C** (Scheme 1).[14] While thermally robust, these MICs *alkylated* at N3 were found to be susceptible to intermolecular rearrangement and/or decomposition pathways involving the alkyl group that limit their synthetic and catalytic applications. Herein, we present a practical synthesis of MICs *arylated* at N3, based on the formal cycloaddition of 1,3-diaza-2-azoniaallenes salts with alkynes or alkyne equivalents. The increased stability of these new MICs enables the synthesis of complexes that were not previously accessible. This is illustrated by the preparation of ruthenium olefin metathesis catalysts of type **F** that display reactivities comparable to that of their NHC-based counterparts **E** in ring-opening and ring-closing reactions.

Results and Discussion

The “abnormal” bonding mode of carbenes **B** was first identified in 2001 by Crabtree *et al.* with the preparation of iridium complexes in which an imidazolium moiety was coordinated not at C2 but “in the wrong way” at C5. [15] Carbenes of this type were dubbed abnormal since no canonical resonance form of the free *a*NHC showing a carbene center can be drawn without introducing charges (see **B′**). This atypical coordination mode features distinct electronic properties, namely greater σ-donation and a predicted decreased π-accepting ability than the corresponding NHCs **A**. Consequently, since 2001, many other complexes bearing *a*NHC ligands have been reported.[11,12a] The bonding situation found in *a*NHCs complexes is also present in adducts or complexes of 1,2,3,4-tetrazol-5-ylidenes,[16] pyrazolin-4-ylidenes,[17] 1,2,3-triazol-5-ylidenes,[18] and 1,2-isoxazol-4-ylidenes (Scheme 2).[19] Since these ligands are in fact mesoionic compounds,[20] we favor the designation of this broad family as mesoionic carbenes (MICs). [14,21]

Stimulated by their promising electronic properties, the fact that Wanzlick-type dimers of MICs have yet to be observed (which points to relaxed steric requirements),[22] and by our success in the isolation of an *a*NHC (**B_1**, Table 1) in the free state,[23] we embarked on the preparation of free 1,2,3-triazol-5-ylidenes **C**.[14] Triazolium salts were quickly identified as ideal precursors of the desired 1,2,3-triazol-5-ylidenes by analogy with the classical deprotonation route used in the preparation of NHCs and related species. Triazoles are conveniently prepared by the Cu-catalyzed alkyne-azide cycloaddition (CuAAC, “click chemistry”),[24] and are readily alkylated at N3 to yield the target triazolium salts. However, attempted deprotonation of the more readily prepared 1,3-dialkyl-1,2,3-triazoliums salts did not lead to the isolation of stable free MICs. For example, treatment of triazolium **$C_a(H^+)$** with potassium *tert*-butoxide in an ethereal solvent did not lead to the desired MIC **C_a** but to the debenzylated triazole **1** (Scheme 3).[25]

We first chose to replace the comparatively fragile alkyl substituent at N1 by more robust aryl groups, but this could not readily be achieved with the synthetic procedure used for **$C_a(H^+)$**. Firstly, the preparation and purification of aryl azides can be cumbersome, and

present safety risks when performed on scale, especially in the case of sterically hindered substrates. As a remedy, we opted for the one-pot conversion of anilines to the desired aryl azides, followed by *in situ* CuAAC as reported by Moses *et al.* [26] Secondly, the alkylation of 1-aryltriazoles requires stronger alkylating agents than the corresponding 1-alkyltriazoles, and consequently alkyl triflates were used in place of alkyl bromides or iodides.[27] As previously reported, these triazolium salts are cleanly deprotonated with either potassium bis(trimethylsilyl)amide or potassium *tert*-butoxide in ethereal solutions. The corresponding crystalline MICs $\mathbf{C_{b,c}}$ are stable enough in the solid state and in dilute solution under an inert atmosphere to allow for their full characterization (Scheme 4).[14] However, more concentrated solutions of the MICs $\mathbf{C_{b,c}}$, alkylated at N3, decompose to give among other products triazoles **2b** and **3**. These results were rationalized in the case of $\mathbf{C_b}$ by an intermolecular nucleophilic attack leading to the intermediacy of the ion pair [**4b**+**5**], a rearrangement reminiscent to that observed for *a*NHC of type **B** bearing an electrophilic group in the 2-position.[28,29] Indeed, our gas-phase calculations (MP2/TZVPP//BP86/SVP) predict that the rearranged product **2b** is energetically more favourable than $\mathbf{C_b}$ by 46.5 kcal·mol^{-1}, and that the ion pair [**4b**+**5**] is located 40.9 kcal·mol^{-1} above the starting materials (e.g. 2 × $\mathbf{C_b}$). Although the intermediate ion pair is rather high in energy, this could be a viable pathway given sufficient charge stabilization in solution. The formation of triazole **3** from $\mathbf{C_b}$ might be ascribed to the incipient protonation of intermediate **5**, while in the case of $\mathbf{C_c}$ a base-induced elimination resulting in the loss of propene is quite likely. In agreement with these hypotheses, MIC $\mathbf{C_c}$ bearing the more sterically hindered and less electrophilic isopropyl group in the 3-position was found to be much more resistant with respect to these decomposition pathways. Nevertheless, the stability of $\mathbf{C_c}$ remained inferior to that of classical NHCs **A**, which hindered its storage in the free state over extended periods (i.e. > weeks). Furthermore, we reached the conclusion that the finite stability of these alkylated MICs was responsible for disappointing results in our primary attempts at preparing MIC transition metal complexes by direct ligand substitution; in particular the synthesis of ruthenium complexes was unsuccessful (*vide infra*).

Synthesis of Arylated MICs

Seeking to improve the stability of MICs **C**, we directed our efforts towards the preparation of 1,3-diarylated-1*H*-1,2,3-triazolium salts of type $\mathbf{C_{Ar}(H^+)}$ (Scheme 5). Evidently, these target precursors, unlike 3-alkyltriazolium salts $\mathbf{C_{a\text{-}d}(H^+)}$, are not accessible from the direct arylation of triazoles at N3. However, Wirschun and Jochims reported the preparation in moderate to good yields of a number of 1,3-diarylated-1*H*-1,2,3-triazolium salts $\mathbf{C_{Ar}(H^+)}$ by the formal 1,3-dipolar cycloaddition between 1,3-diaza-2-azoniaallene salts **H** and alkynes or synthetic alkyne equivalents (Scheme 5).[30,31]

We have found that, under optimized conditions, this reaction is suitable for the preparation of a broad range of 1,3-diaryl-1*H*-1,2,3-triazolium salts $\mathbf{C_{Ar}(H^+)}$. Triazenes **6a-d** were first prepared by an adaptation of different literature procedures, including the treatment of anilines with isoamyl nitrite (**6a,d**),[32] the nucleophilic attack of anilines on arenediazonium salts in pH-buffered aqueous solutions (**6c**),[33] and the nucleophilic attack of aryl Grignards on aryl azides (**6b**).[34] The cycloaddition is then best carried out in a single one-pot operation by the addition of *tert*-butyl hypochlorite (as the N-chlorinating agent) to a stirred suspension of the triazene **6a-d**, alkyne **7a-r**, and potassium hexafluorophosphate in dichloromethane at -78°C. Warming to room temperature, filtration of the insoluble inorganic byproducts, and trituration in diethyl ether affords the desired triazolium salts $\mathbf{C_{xy}(H^+)}$[35] (Scheme 6). It is noteworthy that this formal cycloaddition, unlike CuAAC, proceeds rapidly below room temperature, and does not necessitate copper catalysts. The scope of the reaction is quite broad with respect to the alkyne partner, and tolerates both electron-rich (**7j,l**) and electron-poor (**7f**) alkynes, as well as enynes (**7k**). Highly sterically

demanding triazolium salts can be prepared (**$C_{ac}(H^+)$, $C_{ad}(H^+)$**), although yields are depressed in the most difficult cases, as for *tert*-butylacetylene (**7g**). In addition to terminal alkynes, cycloaddition with internal alkynes also proceeds smoothly (**$C_{an\text{-}ao}^+$**). Trimethylsilyl alkynes participate in this reaction as terminal alkyne surrogates, since protodesilylation occurs readily and the protic triazolium salts are instead obtained (**$C_{aa}(H^+)$, $C_{ae}(H^+)$, $C_{ai}(H^+)$**). As indicated by Wirschun and Jochims,[30] success in the formation of the heterocycle probably depends on the stability of **G** and **H**. For some combinations of triazene and alkyne substrates, we found that the reaction proceeds best at high concentrations in the presence of an excess of alkyne. Occasionally, as is the case for dimesityltriazene **6b**, performing the cycloaddition in the absence of potassium hexafluorophosphate, which presumably shifts the **G-H** equilibrium towards the more stable chlorotriazene, and performing the anion exchange in a subsequent step results in higher yields. Finally, this reaction is readily scaled-up, as exemplified by the preparation of **$C_{bb}(H^+)$** at the 20-mmol scale in excellent yields (10.1 g, 88%).

Since some alkynes are either expensive or less practically accessible, it may be advantageous to use vinyl halides (**8a-q**) as synthetic alkyne equivalents in a cognate preparation of MIC precursors (Scheme 7A). The cycloaddition proceeds under the aforementioned conditions, during which spontaneous elimination of hydrogen halide occurs. Allyl halides (e.g. **9**) can also be used; in this case dehydrohalogenation-aromatization of the intermediate adduct (**10**) is not complete, but is readily achieved by treatment with an amine base in a second step (Scheme 7B).

Treatment of most 1,3-diaryl-1*H*-1,2,3-triazoliums salts **$C_{xy}(H^+)$** with potassium bases such as potassium bis(trimethylsilyl)amide or preferably potassium *tert*-butoxide results in their clean deprotonation and formation of the target stable free MICs **C_{xy}** in moderate to excellent yields (Scheme 8). However, attempted deprotonation of ester- [**$C_{af}(H^+)$**], fluoro- [**$C_{da}(H^+)$** and **$C_{dq}(H^+)$**] and alkenyl-substituted [**$C_{ak}(H^+)$**] triazoliums did not yield the corresponding free MICs. Formation of the free MICs is evidenced by the disappearance of the triazolium CH signal in the ^{1}H-NMR spectra (δ = 8.4-9.4 ppm) and the appearance of a low field signal in the ^{13}C-NMR spectra (δ = 200-206 ppm), typical of carbenes.[36] These signals are comparable to those observed for MICs alkylated at N3 such as **$C_{b\text{-}d}$** (δ = 198-202 ppm). The ethoxy-substituted MIC **C_{aj}** is an exception, and features a ^{13}C-NMR signal at a considerably higher field (δ = 179.6 ppm).

Experimental and Calculated Properties of MICs

The structure of MIC **C_{ag}** was unambigously established by X-ray crystallography (Figure 1). Its structural parameters in the solid state are comparable to those previously reported for the MIC **C_b**, alkylated at N3.[14] Both mesoionic carbenes display a planar ring with bond lengths medial between that of single and double bonds, features indicative of its aromatic character. As previously observed for **$C_b(H^+)$**/**C_b** and most carbenes and their conjugate acids, deprotonation is accompanied by a contraction of the endocyclic angle at the carbene center (**$C_{ac}(H^+)$**: 106°; **C_{ag}**: 100°), which reflects the increased *s*-character of the carbene σ lone pair orbital.[8c,12a]

The free carbenes proved to be very robust and could be stored in the solid state at room temperature under an inert atmosphere for several weeks. In contrast to **$C_{b\text{-}c}$** (Scheme 4), MIC **C_{ba}** (m.p. = 154-156°C dec.) shows no sign of decomposition upon heating in benzene solution for 12h at 50°C. This illustrates the efficacy of introducing aryl substituents at N3 to shut down undesired decomposition pathways. Consistent with previous results,[14] no dimerization of these carbenes was observed in solution.

The electronic properties of the new arylated triazolylidenes were evaluated by preparing the iridium carbonyl complexes **11ac** and **11aj** (Scheme 9). The CO vibration frequencies (**11ac**: ν_{avg} = 2018 cm^{-1}; **11aj**: ν_{avg} = 2020 cm^{-1}) are comparable to those found for complex [(**C$_b$**)Ir(CO)$_2$Cl] (ν_{avg} = 2019 cm^{-1}), and for the analogous iridium complex of a 1,3-dialkylated-1,2,3-triazol-5-ylidene previously reported by Albrecht *et al.* (ν_{avg} = 2021 cm^{-1}).[18d] From these results, it can be concluded that i) the electronic properties of **C$_{Ar}$** are not strongly influenced by the nature of substituents at N1, N3 and C5, and ii) that the donor properties of **C$_{Ar}$** are greater than those of NHCs **A** (ν_{avg} = 2022-2031 cm^{-1}),[37] but lesser than those of *a*NHC **B** (ν_{avg} = 2003-2006 cm^{-1}),[38] and pyrazolin-4-ylidenes (a.k.a. cyclic bent-allenes; ν_{avg} = 2002 cm^{-1}).[17e] The solid-state structure of complex **11ac** (Scheme 9, right) is illustrative of the large steric demands imposed by ligand **C$_{ac}$**, bearing three 2,6-diisopropylphenyl substituents. As a result, the iridium center deviates from coplanarity by 19 ° and is located 0.55 Å above the plane of the heterocycle. The consequence of these steric requirements also manifests itself in the solution NMR spectra with a broadening of peaks indicative of restricted rotation at the NMR timescale for **11ac**, but not for the less hindered **11aj**.

To gain greater insight into the structure and properties of free MICs of type **C**, gradient-corrected density functional theory calculations were performed on models of MIC **C$_b$** alkylated at N3, MIC **C$_{ag}$** arylated at N3, and of the parent MIC **C$_H$** bearing only hydrogen substituents. Molecular geometries were optimized at the BP86/def2-SVP level of theory (hereafter denominated BPI), and single-point energies and bonding analyses were carried out using an extended basis set at BP86/def2-TZVPP//BP86/def2-SVP (BPII) and MP2/def2-TZVPP//BP86/def2-SVP (MPII) levels of theory. Further computational details can be found in the Supporting Information. As can be seen from the caption of Fig. 1, the calculated geometry for **C$_{ag}$** is in excellent agreement with the experimental values. The theoretical data are summarized in Table 1, along with the results for representative carbenes of type **A** and **B**.[23] The stability of MICs of type **C** is corroborated by their large singlet-triplet gap (55.4-59.4 kcal·mol^{-1}), and the correspondingly large HOMO-LUMO gap (note that for **C$_{ag}$**, the triplet state is not an energy minimum; the geometry optimization led to rearrangement of substituents). The stability of **C** derives in part from the sizeable aromatic character, as evidenced by NICS calculations for **C$_H$** (NICS(0)=-14.93; NICS(1)$_{zz}$=-36.06). These indices are comparable to those of other aromatic 5-membered heterocycles including pyrrole, thiophene, and 1,2-pyrazol-4-ylidenes devoid of exocyclic π-donating substituents.[39] The calculations reveal that 1,2,3-triazol-5-ylidenes **C** are higher in energy by 21.6 to 25.9 kcal·mol^{-1} than the corresponding 1,2,4-triazol-5-ylidene isomers (Enders' NHCs).[40] In comparison, the *a*NHC **B$_1$** is only 14.1 kcal·mol^{-1} higher in energy than its normal NHC isomer **A$_1$**.[23] Analysis of the frontier orbitals of **C$_{ag}$** (Figure 2) shows that the HOMO can be characterized as a σ-lone pair at carbon (-4.441 eV), as found in classical NHCs (e.g. **A$_1$**; -5.000 eV) and their abnormal isomers (e.g. **B$_1$**; -4.403 eV). The relative lone pair energy levels are in agreement with the assessment of electronic properties derived from the CO stretching frequencies of [(carbene)Ir(CO)$_2$Cl] complexes. The highest occupied π-orbital is the C4-C5 bonding HOMO-1 (-5.770 eV), which is significantly lower than the HOMO, and exhibits antibonding conjugation with the substituent at C4 as observed for **B$_1$**.[23] The LUMO has a rather small orbital coefficient at C5. The greater partial negative charge [q(C)] for carbenes of type **B** and **C** is consistent with their preferred representation as mesoionic compounds. The calculated second proton affinity is very small;[41] in fact, the second proton would bind at N2 (2nd PA: 55.7-119.3 kcal·mol^{-1}) and not at C5 (1.5-1.6 kcal·mol^{-1}). Finally, the calculated PAs of **C$_b$** (272.5 kcal·mol^{-1}) and **C$_{ag}$** (275.2 kcal·mol^{-1}) are closer to that of imidazol-2-ylidenes [270.4 kcal·mol^{-1} for 1,3-dimesitylimidazol-2-ylidene (IMes)] than to that of **B$_1$** (287.0 kcal·mol^{-1}). Accordingly, the conjugate acids of the first three are experimentally found to be deprotonated with mild alkoxide bases, while the latter requires stronger amide bases.

MIC-Ruthenium Complexes and Olefin Metathesis

Having established the synthesis and electronic structure of several MICs **C**, we turned our attention to their application as ligands. Olefin metathesis with ruthenium-based catalysts, a well-known and synthetically useful reaction, was chosen in order to demonstrate the effectiveness of MICs in a catalytic setting.[3d-h] Previous work has demonstrated that the structure of the ligand can have a profound effect on the reactivity and stability of the catalyst (e.g., $\mathbf{D_1}$ vs. $\mathbf{E_1}$).[3h,42] Furthermore, the use of carbenes with unusual bonding modes or structure such as cyclic amino alkyl carbenes (CAACs) has been shown to affect the selectivity of ruthenium metathesis catalysts.[43]

Free MICs of type **C** bearing flanking aryl groups of varying steric demand were selected for the synthesis by simple ligand substitution of the target complexes of type **F**, which represent MIC-based analogues of the standard NHC-based metathesis catalyst $\mathbf{E_2}$. Early attempts using the MIC $\mathbf{C_d}$ alkylated at N3 (SI) resulted in complete decomposition, but gratifyingly, the use of more robust MICs arylated at N3, $\mathbf{C_{aa}}$, $\mathbf{C_{ab}}$, $\mathbf{C_{ad}}$, and $\mathbf{C_{ba}}$, provided the targets $\mathbf{F_{aa}}$, $\mathbf{F_{ab}}$, $\mathbf{F_{ad}}$, and $\mathbf{F_{ba}}$ (Scheme 10). Combining a free MIC with complex $\mathbf{D_2}$[44] in benzene resulted in 100% conversion after several hours. The resulting complexes were isolated by recrystallization from CH_2Cl_2-pentane ($\mathbf{F_{aa}}$, $\mathbf{F_{ab}}$, $\mathbf{F_{ba}}$) or pentane ($\mathbf{F_{ad}}$) at -30 °C without the need for column chromatography. The complexes were found to decompose relatively quickly in solution upon exposure to oxygen, but were indefinitely stable in the solid state under an inert atmosphere. NMR spectroscopy studies on the ligand displacement reaction with $\mathbf{D_2}$ indicated that a MIC-phosphine complex, where the MIC initially displaces the chelating ether moiety, was formed before subsequently yielding the desired complex. [45] This intermediate usually persisted for several hours before forming the desired complex.

Complexes $\mathbf{F_{aa}}$ and $\mathbf{F_{ad}}$ were characterized by single crystal x-ray diffraction (Figure 3). Bond lengths in $\mathbf{F_{aa}}$ and $\mathbf{F_{ad}}$ are very similar to those found in $\mathbf{E_2}$. The MIC carbon-Ru bond length (1.99 Å versus 1.98 Å in $\mathbf{E_2}$), benzylidene C-Ru bond length (1.82 Å versus 1.82 Å), and the O-Ru bond length (2.27 Å versus 2.26 Å) are largely conserved across the three species.[46] Notably, the smaller aryl substituent (on C4 in $\mathbf{F_{aa}}$, and N1 in $\mathbf{F_{ad}}$) is positioned above the Cl-Ru-Cl plane in order to minimize steric interactions with the chlorines, while the larger substituent is positioned above the benzylidene.[47]

To evaluate the catalytic activity of these complexes, they were subjected to several standard metathesis screens.[48] Catalysts $\mathbf{F_{aa}}$, $\mathbf{F_{ab}}$, and $\mathbf{F_{ba}}$ showed good ring-opening metathesis polymerization (ROMP) activity (Figure 4), while catalyst $\mathbf{F_{ad}}$ only reached low conversions, even after a period of several days. Comparing the ROMP conversion profiles of MIC-based catalysts to standard catalyst $\mathbf{E_2}$ reveals a few similarities and differences. For instance, $\mathbf{F_{ab}}$ shows an almost identical conversion profile to $\mathbf{E_2}$ while $\mathbf{F_{ba}}$ is slightly slower, but still relatively fast, and $\mathbf{F_{aa}}$ is much slower, although it does reach 100% conversion after ca. 1h.

The most surprising result is the difference in reactivity between catalysts $\mathbf{F_{aa}}$ and $\mathbf{F_{ab}}$, since the only difference between the two is the substitution of a mesityl group for a phenyl at C4. We hypothesized that the observed behavior might be largely due to a difference in initiation rates and, in order to probe this, we constructed several Eyring plots for the reaction of each catalyst with butyl vinyl ether.[42a,49] The results for the initiation parameters are given in Table 2.

Catalysts $\mathbf{F_{aa}}$, $\mathbf{F_{ab}}$, $\mathbf{F_{ba}}$, and $\mathbf{F_{ad}}$ all exhibited a negative $\Delta S^{\ddagger}$, which is consistent with an associative or associative interchange initiation mechanism previously reported for catalysts incorporating a Hoveyda-type chelate.[50] Interestingly, while catalysts $\mathbf{F_{aa}}$ and $\mathbf{F_{ad}}$ were found to have very similar activation entropies, catalysts $\mathbf{F_{ab}}$ and $\mathbf{F_{ba}}$ differed by ca. 10 eu

from these. Furthermore, the activation enthalpy for $\mathbf{F_{aa}}$ was found to be lower than that for $\mathbf{F_{ab}}$. Nevertheless, a 1.4 kcal·mol^{-1} difference in $\Delta G^{\ddagger}$ between $\mathbf{F_{aa}}$ and $\mathbf{F_{ab}}$ was observed when combining the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ parameters at RT. This difference accounts nicely for the observed variations in initiation, while also explaining the almost complete inactivity of catalyst $\mathbf{F_{ad}}$ at RT. Unfortunately, while it is clear that sterics play a significant role in catalyst initiation, so far a qualitative model which accounts for the observed differences in initiation, particularly between $\mathbf{F_{aa}}$ and $\mathbf{F_{ab}}$, has eluded us.[51]

Following the initiation studies, the performance of each catalyst in RCM was assessed (Figure 5). Again, catalyst $\mathbf{F_{ad}}$ was found to be almost completely inactive at 30°C. Other catalysts displayed conversion profiles consistent with their initiation activation energies. For instance, $\mathbf{F_{ab}}$ shows a fast increase in conversion followed by a plateau that most likely results from catalyst decomposition. On the other hand, $\mathbf{F_{aa}}$ exhibits an induction period characteristic of a slow initiation followed by a gradual increase towards 100% conversion. Notably, even though $\mathbf{F_{aa}}$ initiates at a slower rate than $\mathbf{F_{ab}}$, it is able to reach 100% conversion under the examined conditions while $\mathbf{F_{ab}}$ is not. For this assay, $\mathbf{F_{ba}}$ appears to be the best catalyst as it displays fast initiation and good stability throughout the reaction. In fact, $\mathbf{F_{ba}}$ closely matches the performance of $\mathbf{E_2}$.

To further examine the differences in reactivity between the catalysts, trisubstituted RCM was attempted (Figure 6). As expected, $\mathbf{F_{aa}}$ and $\mathbf{F_{ab}}$ exhibited the same behavior as stated above, with $\mathbf{F_{aa}}$ displaying a lengthy induction period while $\mathbf{F_{ab}}$ begins conversion to product almost immediately. Catalyst $\mathbf{F_{ab}}$ reached a maximum conversion of ca. 50%, while $\mathbf{F_{aa}}$ was able to reach 100% conversion after a period of ca. 16 h. These results confirm that not only does the change from a Ph ($\mathbf{F_{aa}}$) to Mes ($\mathbf{F_{ab}}$) have a profound effect on the initiation rate, but that it also impacts the relative stability of the catalysts. Catalyst $\mathbf{F_{ba}}$ was relatively sluggish over the time period examined but was able to reach 100% conversion after ca. 24 h at 30°C. Overall, in the trisubstituted RCM assay, the MIC-based catalysts were clearly inferior to $\mathbf{E_2}$, in contrast to the previous assays where they displayed comparable activity.

Conclusions

The presence of N-alkyl substituents was found to be a predominant factor limiting the stability of 1*H*-1,2,3-triazol-5-ylidenes **C**. Introduction of N-aryl substituents in place of these alkyl groups vitiates these decomposition pathways, and results in MICs exhibiting stabilities approaching that of NHCs **A**. A wide variety of 1,3-diaryl substituted MICs are conveniently prepared through the scalable Wirschun-Jochims formal cycloaddition between 1,3-diaza-2-azoniaallene salts and alkynes or synthetic alkyne equivalents, followed by deprotonation with mild alkoxide bases. By this method, MICs bearing highly sterically demanding (Tipp, *t*Bu), as well as polar and functionalized substituents in α-position to the carbene center can be obtained. The enhanced stability of N-arylated MICs allows for the preparation of ruthenium olefin metathesis catalysts by simple ligand substitution. MICs-bearing ruthenium benzylidene complexes **F** are proficient room-temperature catalysts for the ring-opening metathesis polymerization of cyclic olefins, and for ring-closing olefin metathesis reactions leading to both di- and trisubstituted cylic alkenes. The catalytic properties of the MIC-Ru complexes **F**, in particular with respect to their rates of initiation and resistance to deactivation, are strongly influenced by the nature of the MIC substituents, and in several cases may rival the performance of well-established NHC ruthenium olefin metathesis catalysts **E**. The combination of their practical, versatile and modular preparation, enhanced stability, advantageous electronic properties, and the demonstration of their effectiveness in a catalytic setting foreshadow the development of numerous MIC transition metal complexes for catalytic applications.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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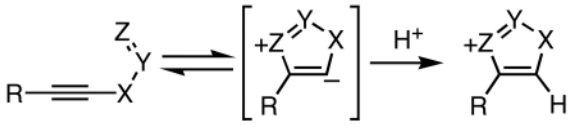

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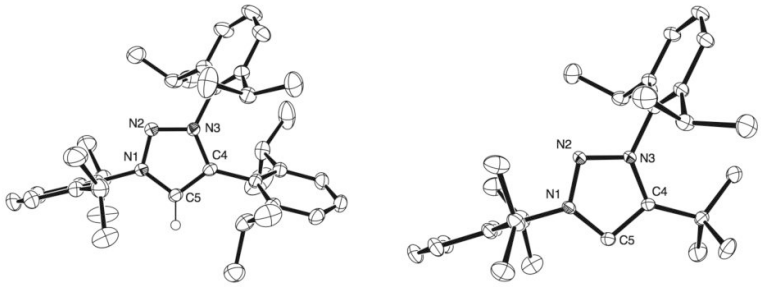


Figure 1.

Solid-state structures of $\mathbf{C_{ac}(H^+)}$ (left) and $\mathbf{C_{ag}}$ (right) with thermal ellipsoids drawn at 50% probability. For clarity, counter-ions and hydrogen atoms, except for the ring hydrogen of $\mathbf{C_{ac}(H^+)}$ were omitted. Calculated values for $\mathbf{C_{ag}}$ (BPI, see text for details) are given in italics. Selected bond lengths (Å) and angles (°) for $\mathbf{C_{ac}(H^+)}$: N1-N2: 1.3201(16), N2-N3: 1.3278(16), N3-C4: 1.3819(16), C4-C5: 1.3713(19), C5-N1: 1.3523(17), ∠N1-C5-C4: 106.36(12). $\mathbf{C_{ag}}$: N1-N2: 1.3420(7)/*1.352*, N2-N3: 1.3302(7)/*1.334*, N3-C4: 1.3763(8)/*1.396*, C4-C5: 1.4041(8)/*1.414*, C5-N1: 1.3655(8)/*1.373*, ∠N1-C5-C4: 100.21(5)/*100.8*.

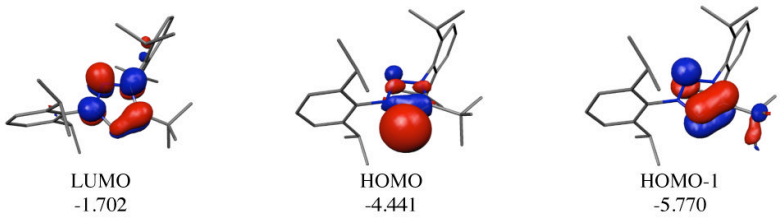


Figure 2.
Frontier orbitals of $\mathbf{C_{ag}}$ and orbital energies in eV at BPI level of theory.

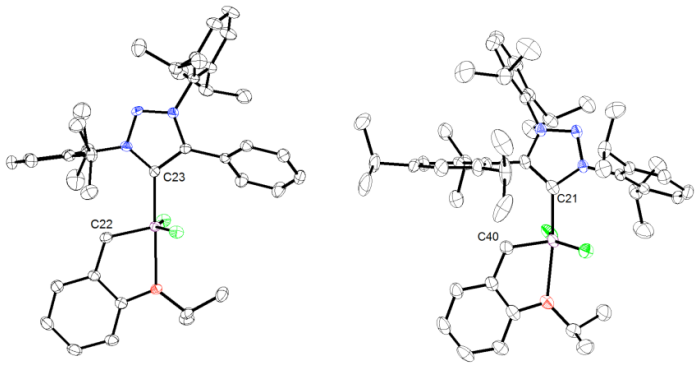


Figure 3.
Solid-state structures of $\mathbf{F_{aa}}$ (left) and $\mathbf{F_{ad}}$ (right) with thermal ellipsoids drawn at 50% probability. Selected bond lengths (Å) for $\mathbf{F_{aa}}$: C23-Ru: 1.9913(1), C22-Ru: 1.8235(1), O-Ru: 2.2696(1). For $\mathbf{F_{ad}}$: C21-Ru: 1.9852(1), C40-Ru: 1.8157(1), O-Ru: 2.3176(1).

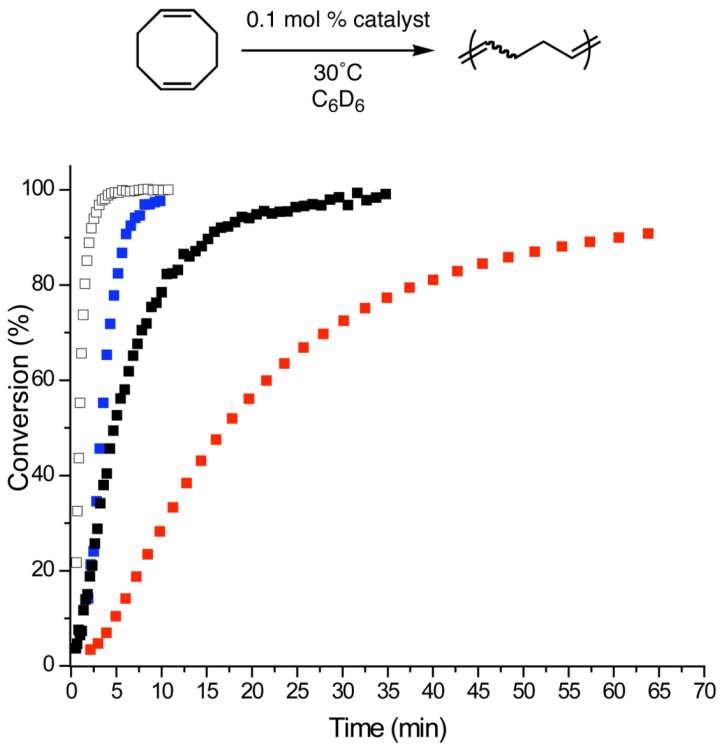


Figure 4.
ROMP of COD with catalysts $\mathbf{F_{aa}}$ (red), $\mathbf{F_{ab}}$ (blue), $\mathbf{F_{ba}}$ (black), and $\mathbf{E_2}$ (white). Conditions: 0.1 mol% catalyst, 30°C, 0.1 M (substrate) in C_6D_6.

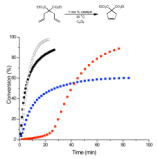


Figure 5.
RCM performance of catalysts $\mathbf{F_{aa}}$ (red), $\mathbf{F_{ab}}$ (blue), $\mathbf{F_{ba}}$ (black), and $\mathbf{E_2}$ (white). Conditions: 1 mol% catalyst, 0.1 M substrate, 30°C, in C_6D_6.

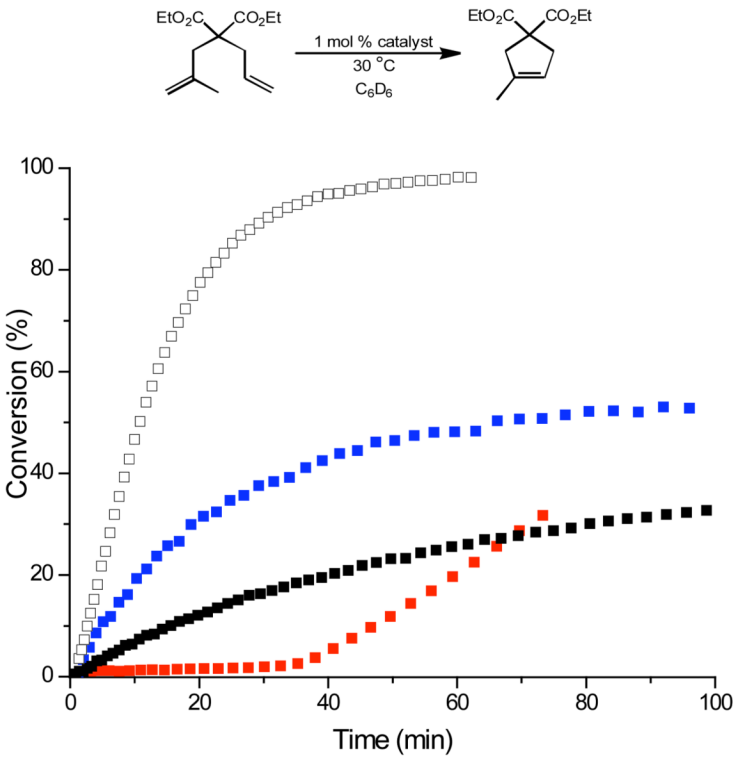
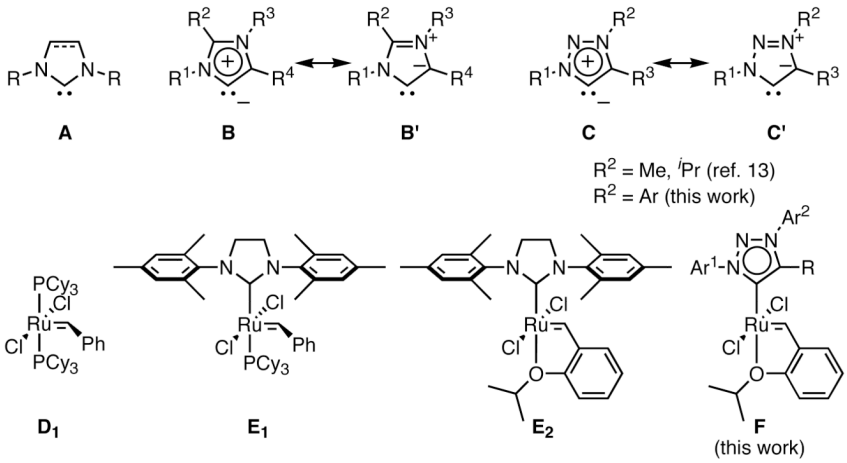
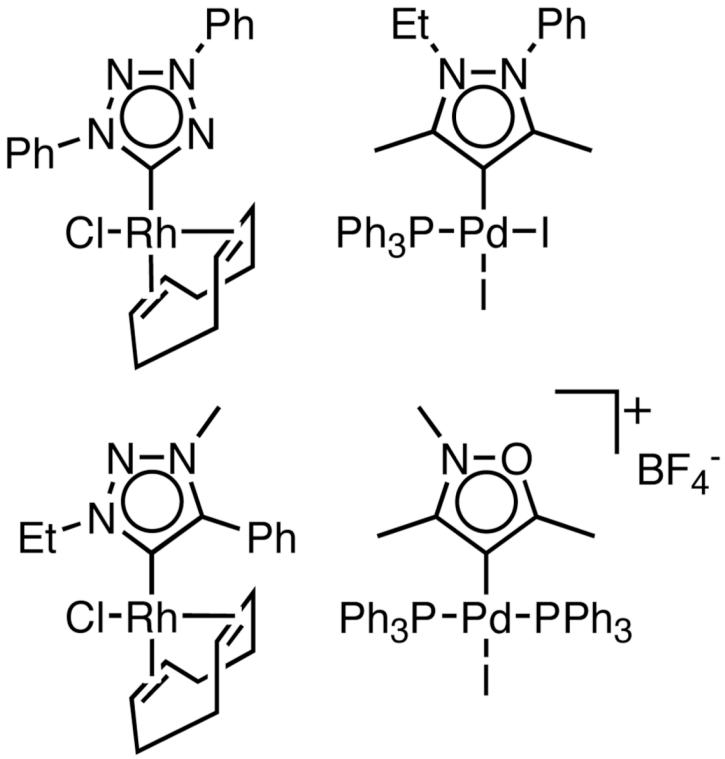


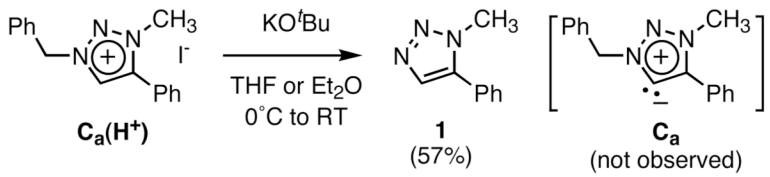
Figure 6.
Tri-substituted RCM performance for catalysts $\mathbf{F_{aa}}$ (red), $\mathbf{F_{ab}}$ (blue), $\mathbf{F_{ba}}$ (black), and $\mathbf{E_2}$ (white). Conditions: 1 mol% catalyst, 0.1 M in substrate, 30°C, in C_6D_6.



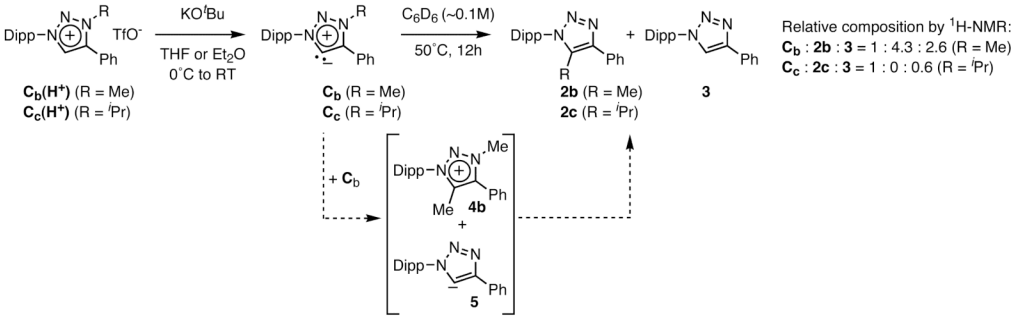
Scheme 1.
Classes of compounds discussed in this manuscript.



Scheme 2.
Examples of complexes of mesoionic carbenes.[16-19]



Scheme 3.
Attempted deprotonation of 1,3-dialkyl-1,2,3-triazolium salt $\mathbf{C_a(H^+)}$.



Scheme 4.

Preparation and decomposition of 3-alkyl-1,2,3-triazol-5-ylidenes.[14, [a]]

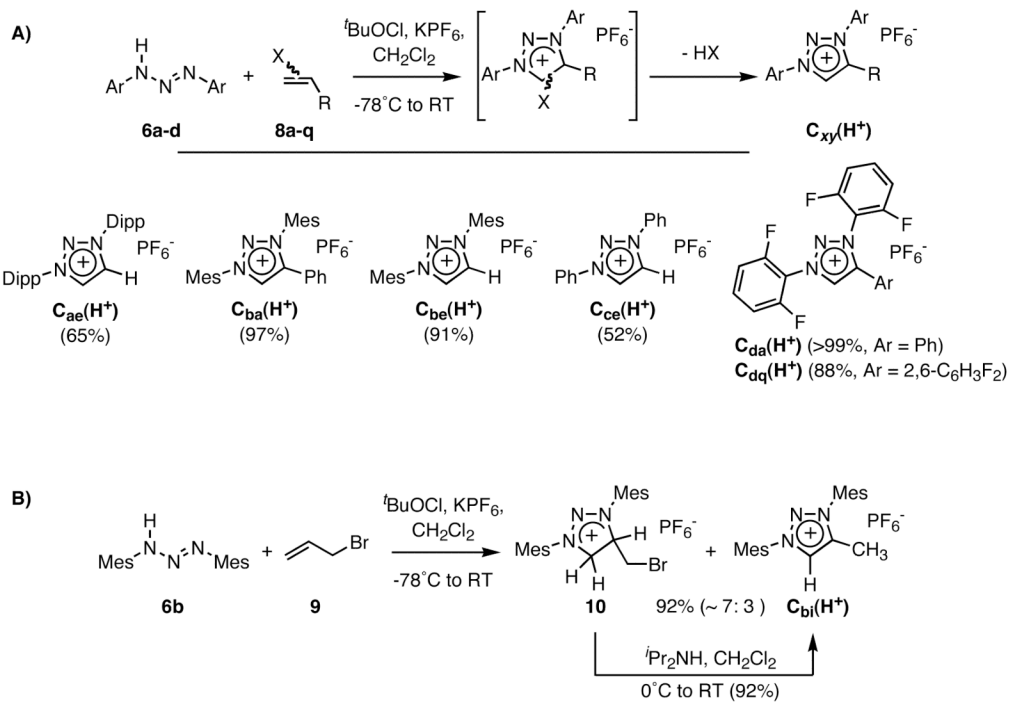
[a] Dipp = 2,6-diisopropylphenyl

Scheme 5.

Triazolium salts from the formal cycloaddition of 1,3-diaza-2-azoniaallene salts **H** and alkynes according to Wirschun and Jochims.[30]

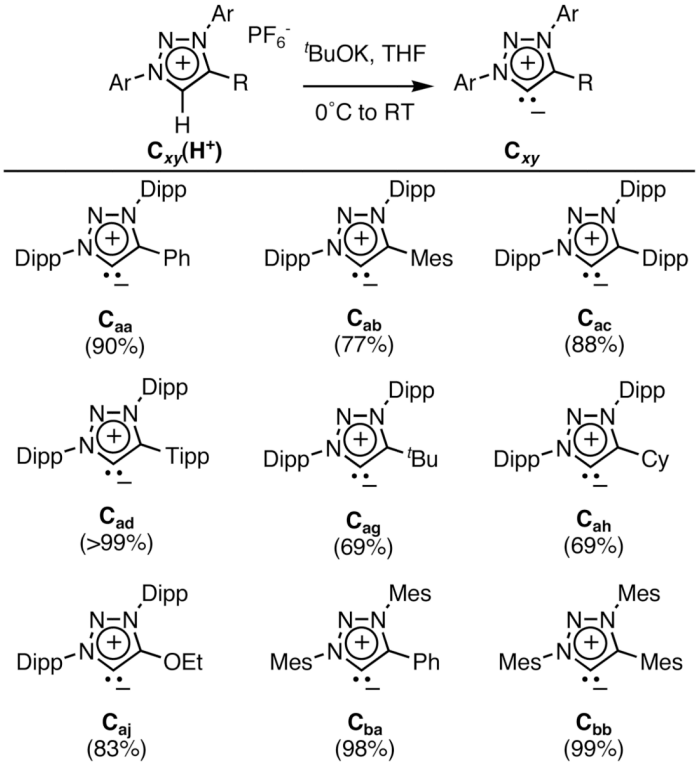
Scheme 6.

Preparation of 1,3-diaryl-1,2,3-triazolium salts from triazenes and alkynes.
[a]Performed with either PhCCH (**7a**) or $PhCCSiMe_3$ (**7r**); [b]With Me_3SiCCH (**7e**); [c]With $CH_3CCSiMe_3$.



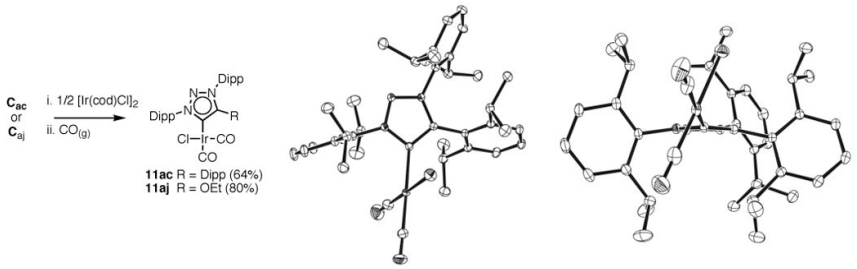
Scheme 7.

Preparation of 1,3-diaryl-1,2,3-triazolium salts from triazenes and synthetic alkyne equivalents.



Scheme 8.

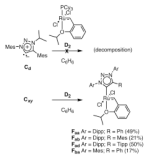
Preparation of MICs $\mathbf{C}_{xy}$ by deprotonation of triazolium precursors $\mathbf{C}_{xy}(\mathbf{H}^+)$.



Scheme 9.

Preparation of iridium carbonyl complexes.

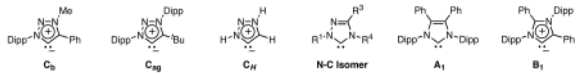
Center and Right: Molecular views of **11ac** in the solid state under different angles, with thermal ellipsoids drawn at 50% probability. For clarity, hydrogen atoms were omitted.



Scheme 10.
Synthesis of ruthenium complexes by ligand substitution.

Table 1

Calculated properties of MICs and related carbenes.[a]



	HOMO (eV)[b]	HOMO/LUMO Gap[b]	S/T Gap[c]	E_{rel} N-C isomer[d]	1st PA[d]	2nd PA[d]		q(C)[e]
					C5	C5/C5	C5/N2	
C_b	-4.484	55.0	55.9	-21.6	272.5	1.6	109.8	-0.12
C_{ag}	-4.441	63.2	*[f]*	-22.7	275.2	1.6	119.3	-0.14
C_H	-4.527	62.3	59.4	-25.9	252.8	1.5	55.7	-0.16
A_1[23]	-5.000[c]	-	-	-	*[g]*	*[h]*	-	*[i]*
B_1[23]	-4.403[c]	-	-	-	287.0	144.6	-	*[j]*

[a] All energies in kcal·mol^{-1} unless otherwise mentioned.

[b] BPI.

[c] BPII.

[d] MPII.

[e] NBO results with BPII.

[f] Structural optimization of the triplet structure always resulted in H-transfer to C5.

[g] Normal imidazolium NHCs 1st PA at C2 range from 228.9 to 274.9 kcal·mol^{-1}; for IMes: 270.4 kcal·mol^{-1}.[41]

[h] Normal imidazolium NHCs 2nd PA at C2 range from 38.9 to 106.5 kcal·mol^{-1}; for IMes: 105.3 kcal·mol^{-1}.[41]

[i] Partial charges at carbene center q(C) for normal imidazolium NHCs range from -0.01 to 0.08; for IMes: 0.08.[41]

[j] Abnormal imidazolium NHCs q(C) range from -0.16 to -0.19; for 1,3-dimesitylimidazol-5-ylidene (*a*IMes): -0.17.[41]

Table 2

Comparison of activation parameters for catalysts **F_{aa}, F_{ab}, F_{ad}, and F_{ba}**.[a]

Catalyst	$\Delta G^{\ddagger}_{298}$ (kcal·mol^{-1})	$\Delta H^{\ddagger}_{0}$ (kcal·mol^{-1})	$\Delta S^{\ddagger}$ (eu)
F_{aa}	21.6 ± 0.8	12.1 ± 0.5	-31.9 ± 1.5
F_{ab}	20.2 ± 0.2	13.5 ± 0.8	-22.5 ± 2.7
F_{ad}	23.5 ± 0.1	13.6 ± 0.6	-33.0 ± 1.9
F_{ba}	20.8 ± 0.3	14.6 ± 0.5	-21.0 ± 1.6

[a] Conditions: catalyst (0.003 mmol), butyl vinyl ether (0.09 mmol, 0.15 M) in d8-toluene at varying temperatures.